# CLEAN GAS TURBINE FUEL FROM PETROLEUM COKE

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Keywords: Petrleum coke, partial oxidation and gasification

## Introduction

Oil refiners in the United States often rely on coking to reject excess carbon from heavier crudes, resulting in an ever-increasing supply of petroleum coke. Marketing of coke as a fuel is hampered by its high sulfur and metals content which makes it unsuitable for conventional combustors. Several major IGCC projects, based on the low value refinery stocks, are currently progressing through detailed engineering, procurement and construction (1).

In a cost-shared contract with DOE/PETC, Bartlesville, The M. W. Kellogg Company has been investigating the gasification and combustion of high-carbon containing refinery by-products using a laboratory-scale fluidized bed and a sub-pilot scale transport reactor located at Kellogg's Technology Development Center where both fluid bed and transport reactors have been developed for coal gasification (2). The transport reactor process pioneered by The M. W. Kellogg Company, makes use of enriched air to partially oxidize and gasify the petroleum coke. Results of the laboratory and pilot plant program are presented in the paper along with proposed process flow diagram that incorporates some recent advances made in sulfur removal and recovery.

The objective of the study was to develop a process to convert high-carbon refinery byproducts such as petroleum coke and ROSE™ (Residuum Oil Supercritical Extraction) pitch to fuel gases suitable for power generation. Experiments were conducted in the transport reactor (TRTU) to study partial oxidation, gasification and devolatilization of the coke at temperatures up to 1800°F in a continuous mode. In order to extend the data obtained in the TRTU to higher process temperatures (1850 to 2250°F), experiments were conducted in the Bench-scale Reactor Unit (BRU) to study partial oxidation and gasification in a batch mode. The BRU is capable of heating a bed of solids up to 2250°F and above with oxidant injection.

## Experimental

**Description of Bench-scale Reactor Unit:** A simplified flow schematic of the BRU test facility is shown in Fig. 1. It consists of a 2.067-in. inside diameter (i.d.) section of 10-in. height and an expanded section of 3.068-in. i.d. of 12-in. height. It is made of Incoloy 800H alloy and consists of some ancillary equipment including a steam supply system. The reactor is surrounded by two independently-controlled electrical heaters (for top and bottom zones) and contained within a pressure vessel. Only a small pressure differential is used across the hot reactor vessel. The feed gas is electrically preheated. Product gas leaves the reactor, and is sent to a water-cooled condenser and then to a particulate filter. Water collected in the knockout drum is periodically drained from the unit. An on-line GC, that requires 12 min to complete the gas analysis, is connected to the BRU for gas analysis. It is possible to analyze the concentration of hydrocarbons and carbon oxides ($CH_4$, $C_2H_4$, $C_2H_6$, CO, $CO_2$, $H_2$, $N_2$ and the unsaturates) in the effluent gas of the BRU by using gas sample bags. The BRU facility can be operated at temperatures up to 1950°F at pressures up to 450 psig. A particulate filter, maintained at a temperature of 600 to 700°F, was used to capture the fines for analysis of vanadium and nickel which are present in the coke feed.

Petroleum coke was subjected to partial oxidation (POX) in the BRU over a peak temperature range of 1850 to 2250°F. The tests involved heating the bed to a base temperature followed by introducing the oxidant. Within a short period, the bed temperature reached a peak value and then stabilized or decreased gradually. Tests on combined POX and steam gasification and tests with steam gasification only were performed in the BRU.

**Description of Transport Reactor Test Unit (TRTU)**

A simplified sketch of the reactor system, shown in Fig. 2, consists of a mixing zone, a riser, a cyclone, and a standpipe. The mixing zone of the reactor, which can be operated either as a dense-phase fluid bed or as an entrained reactor, consists of a 10-foot tall section of 1.338 in. i.d. Solids from the standpipe are returned to the bottom of this zone. Fluidization gas, which can be air, $O_2$, steam, $N_2$, or any combination of these, is fed to the bottom of the mixing zone through a gas distributor. During standby periods, mixture of steam and $N_2$ was used. During testing, the steam flow was maintained and $N_2$ to the mixing zone was replaced with air.

Above the mixing zone is a 32-foot tall riser of 0.815 in. i.d. At the base of the riser is an injection nozzle that is used for feeding petroleum coke. At velocities of 15 to 30 ft/s used during partial oxidation/gasification, the gas residence time was about 1 to 2 sec in the riser. Gas and solids leaving the top of the riser flow to a high-efficiency cyclone, that separates the solids and returns them, via the standpipe, to the mixing zone. Gas leaving the top of the cyclone is cooled, measured, and sampled for analysis.

The standpipe consists of a 33-foot tall section with the same i.d. as the mixing zone. The use of a relatively small diameter standpipe requires a low solids inventory and minimal solids holdup time. Fresh solids are added for make-up, if necessary, to the top of the standpipe to compensate for attrition losses. Solid samples are withdrawn from the bottom of the standpipe. Solids are returned to the bottom of the mixing zone via a lateral leg that is aerated.

The nominal size cuts of coke used in the TRTU and the BRU were 40x140 and 40x80 mesh, respectively. The proximate analysis of the petroleum coke (wt%) was: volatile matter-9.4%, fixed carbon-89.6%, moisture-0.5% and ash-0.5%.

**Results and Discussion**

**Testing in BRU**

Tests were conducted in the BRU, in a batch mode, using a bed weight of 200 gm of Lyondell/Citgo petroleum coke with an $O_2$ concentration range of 15 to 30 vol% in nitrogen over an initial temperature range of 1800 to 1950°F at pressure of 100 psia. The peak bed temperature varied from 1850 to 2250°F. Results from fluidized bed testing show that a sulfur- and metals-free gas, suitable as a gas turbine fuel, can be produced from petroleum coke. The gas residence time in the BRU is about the same as in the TRTU, and hence the BRU results are applicable to the TRTU. The $CO/CO_2$ ratio was observed to be a function of $O_2$ partial pressure and temperature. At 30% $O_2$ concentration and 2000°F, the $CO/CO_2$ ratio was found to be 3.5. This was the highest ratio that was obtained over the temperature range and $O_2$ concentrations investigated. The steam gasification rate was determined to be 0.5 lb/lb.hr. The carbon partial oxidation reactions and the carbon gasification reaction in the presence of steam are represented by $C + O_2 \longrightarrow CO_2$; $C + CO_2 \longrightarrow 2CO$; and $C + H_2O \longrightarrow CO + H_2$.

It was also determined that the carbon consumption rate by the combined partial oxidation and gasification by steam is the sum of individual rates obtained in the two processes. The water gas shift reaction was found to be at equilibrium. The devolatilization of coke was studied in the TRTU at a lower temperature, but not in the BRU.

The bed and filter samples obtained at the end of tests were analyzed for vanadium in order to determine if it accumulates in the fines produced during testing. Runs 22 through 25 were done at lower temperatures and the results, presented in Table 1, show that the vanadium present in the feedstock does accumulate in fines. Hence, it should be possible to remove vanadium during coke processing via the fines generated. The nickel content in the bed and filter samples is not meaningful as the thermocouples used in the BRU tests had an Incoloy 800 (high nickel alloy) sheath and were corroded during the tests as a result of high temperatures. In future BRU tests, the thermocouples will be protected by ceramic tubes so that the bed and fines can be analyzed for nickel. Surface areas of fresh and bed samples of petroleum coke from BRU tests were measured by $N_2$ absorption (BET method). The results are given in Table 2.

The above measurements show up to a ten-fold increase in BET surface area as carbon is converted. After a significant carbon conversion is achieved, the coke partial oxidation rate increases since it becomes more reactive due to the increased surface. Thus, a transport reactor is most efficient in processing coke due to staging which utilizes all the $O_2$ to react with solid carbon to produce CO and $CO_2$ without burning volatiles. The recirculating solids have a significantly higher carbon conversion and, so, are more reactive than the fresh feed. Therefore, the coke consumption rate is higher in a transport reactor compared to a fluidized bed.

The temperatures measured in the bed and the gas composition determined using infrared analyzers in test 26 are shown in Fig. 3 and 4. The bed temperature, after reaching a peak value gradually decreased with time showing that the carbon consumption rate increased steadily. The gas composition measured using a GC is also shown in Fig. 4. Additional results, shown in Table 3, indicate that the steam gasification rate is very low as shown by the low conc. of $H_2$ and that the carbon consumption (cons.) rate increases by a factor of nine as the carbon in the bed is consumed.

The gas composition and temperatures measured in test 22 at a nominal bed temperature of 1900°F are shown in Fig. 5 and 6, respectively. These results show that the $CO/CO_2$ ratio is very low at this temperature. Results obtained at an $O_2$ concentration of 30% at initial bed temperature of 1950°F are shown in Table 4. Results for sample 1 correspond to $O_2$ conc. of 40% which was used for a short period as the peak temperature reached 2300°F.

***Testing in TRTU***

Petroleum coke was processed with riser and mixing zone densities of 4 and 14 $lb/ft^3$, respectively at a solid circulation rate of about 600 lb/hr in the TRTU in both partial oxidation and steam gasification modes at temperatures close to 1800°F. These tests confirmed that the inability of operating the TRTU at temperatures exceeding 1800°F prevented complete thermal cracking of volatiles produced, causing coke-like deposits to be formed in the reactor.

Testing in the TRTU showed that the fuel gas produced at temperatures lower than 1800°F has a $CO/CO_2$ ratio less than or equal to 0.5. This gas has a very low heating value and is not suitable for power generation. The partial oxidation and gasification of petroleum coke could not be studied at higher temperatures in this unit due to equipment limitations. The devolatilization of coke was also studied at temperature of 1800°F and yielded a $H_2/CH_4$ molar ratio of 4.0.

A product gas heating value of 124 BTU/scf was estimated for a transport gasifier with enriched air-blown (30% oxygen) mode of operation utilizing the results obtained in the BRU and the TRTU.

**Flowsheet Development / Process Advantages**

Based on the results obtained in the BRU and the TRTU, the process flow diagram, shown in Fig. 7, has been developed to partially oxidize/gasify petroleum coke. This flow diagram incorporates the direct sulfur recovery process, developed by Research Triangle Institute, as this process was deemed best suited for this application. It also incorporates a transport desulfurizer and a transport regenerator for sulfur removal from the product gas. These two units were developed recently by The M.W. Kellogg Co. for the Sierra Pacific project and will be demonstrated shortly. A detailed flowsheet, based on the above flow diagram to generate power from the fuel gas produced from gasification and partial oxidation was developed. Economic analysis of the proposed process is in progress.

The advantages of a transport gasifier over entrained gasifiers, which are being demonstrated to process petroleum coke and other refinery waste streams such as API wastes, acid-soluble oils from alkylation unit, and waste water treatment sludges, are the following:

- It has appreciable carbon inventory while there is none in an entrained gasifier. This factor makes the transport reactor safer and easier to operate.
- Individual refinery waste streams can be injected at different locations where as in an entrained gasifier, these have to be mixed with the main feedstock. The need

for mixing poses significant disadvantages for the latter depending upon the feedstreams.

- There is no short term need for balancing carbon, hydrogen and oxygen in the transport gasifier due to substantial carbon inventory where as it becomes essential to maintain this balance in an entrained gasifier.
- It is thermally more efficient due to a lower operating temperature with less material constraints compared to entrained gasifiers.
- The feeding of petroleum coke can be staged so that the combustion of volatile matter can be prevented in order to increase the heating value of the fuel gas produced. This is not feasible in entrained gasifiers.

**Summary**

At temperatures close to 2000°F, a $CO/CO_2$ molar ratio of 3.5 in the product gas was obtained in the BRU. This shows a great improvement in the gas composition over a value of 0.5 obtained in the TRTU at temperatures lower than 1750°F, and that a temperature of 2000°F is required to process petroleum coke to produce a fuel gas of acceptable heating value. A fuel gas heating value of 124 BTU/scf is estimated for a commercial transport gasifier based on these results. These results were used to develop a flowsheet, and a conceptual design for the transport reactor has been completed to perform economic analysis.

**References**

(1) D. L. Heaven, "Gasification Technologies and World Wide Refining Trends," Presented at NPRA Annual Meeting, San Antonio, March 17-19, 1996.
(2) H. Simons and W. Campbell, "Status of Kellogg's Fluid Bed and Transport Gasification processes," Presented at Institution of Chemical Engineers Conference on Gasification, London, England, November, 1995.

**Abbreviations**

| | |
|---|---|
| BRU | bench-scale reactor unit |
| BET | Brunauer, Emmett, and Teller method based on nitrogen adsorption |
| DOE | Department of Energy |
| DSRP | direct sulfur recovery process |
| FCC | fluid catalytic cracker |
| GC | gas chromatograph |
| PG | Product Gas |
| POX | Partial oxidation |
| PETC | Pittsburgh Energy Technology Center |
| ROSE™ | Residuum Oil Supercritical Extraction |
| TRTU | Transport Reactor Test Unit |

Table 1 - Analyses of bed and filter samples from BRU tests

| Run number | Sample | Vanadium, ppm |
|---|---|---|
| Run 26 | filter | 42,255 |
| | bed | 5,760 |
| Run 25 | filter | 61,710 |
| | bed | 4,888 |
| Run 24 | filter | 14,891 |
| | bed | 4,362 |
| Run 23 | filter | 19,875 |
| | bed | 9,838 |
| Run 22 | filter | 32,873 |
| | bed | 5,843 |
| | Fresh | 1,752 |

Table 2 - Surface Areas of Bed Samples

| Sample | Surface area ($m^2$/gm) |
|---|---|
| 24 | 9.7 |
| 25 | 5.7 |
| 26 | 2.6 |
| Fresh | 0.9 |

Table 3 - Petroleum Coke POX Studies - (Test 26)

| | sam. 1 | sam. 2 | sam. 3 | sam. 4 | sam. 5 |
|---|---|---|---|---|---|
| time, min | 4 | 16 | 29 | 42 | 55 |
| bed temp upper, °F | 2300 | 2147 | 2101 | 2034 | 1987 |
| $H_2$, vol% | 0.97 | 0.21 | 0.14 | 0.11 | 0.12 |
| CO, vol% | 30.6 | 27.1 | 29.3 | 29.2 | 34.4 |
| $CO_2$, vol% | 5.0 | 13.2 | 12.9 | 11.9 | 9.3 |
| $CO/CO_2$ ratio | 6.14 | 2.05 | 2.27 | 2.46 | 3.72 |
| C cons.,gm/min | 2.18 | 2.71 | 2.93 | 2.80 | 3.11 |
| C cons. rate, 1/min | 0.01 | 0.02 | 0.03 | 0.04 | 0.09 |

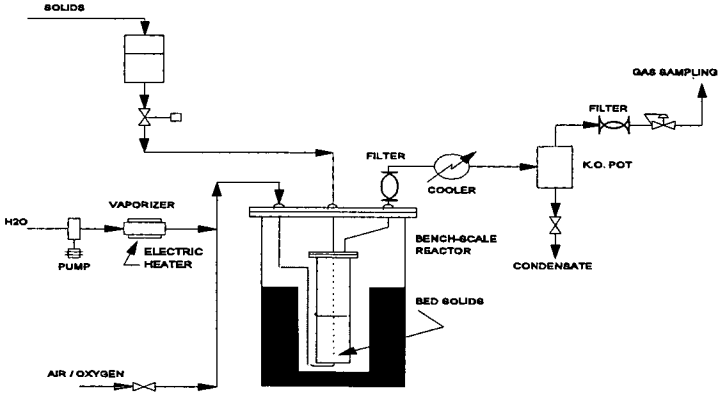


**Fig. 1 Bench-scale Reactor Unit for Petroleum coke Processing**

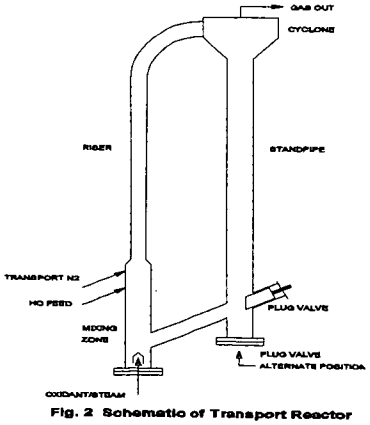


**Fig. 2 Schematic of Transport Reactor**

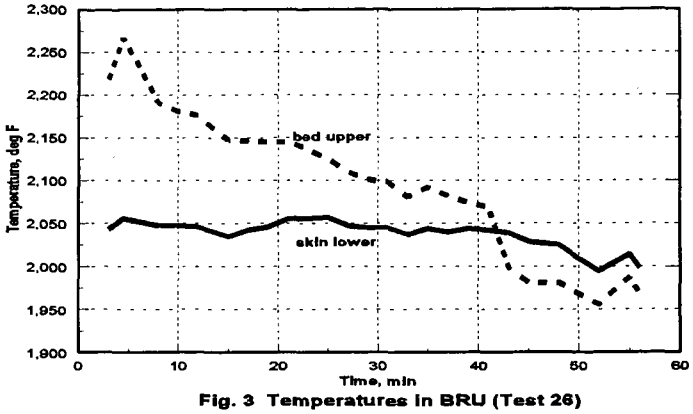


**Fig. 3 Temperatures in BRU (Test 26)**

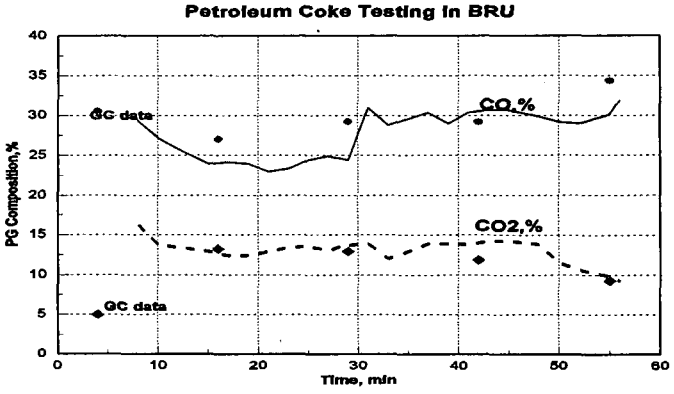


**Fig. 4 PG Analysis as per IR analyzers and GC**

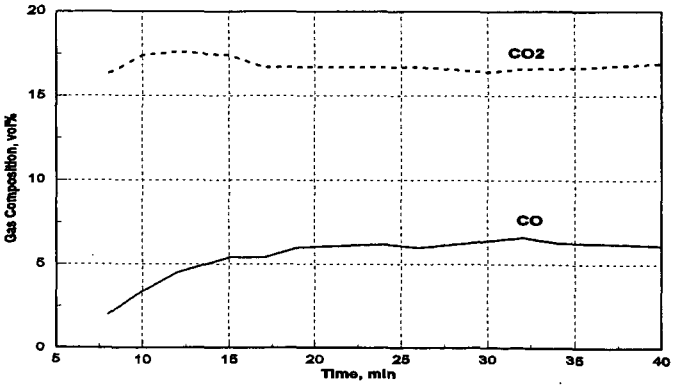


**Fig. 5 Product Gas Composition - Test 22A**

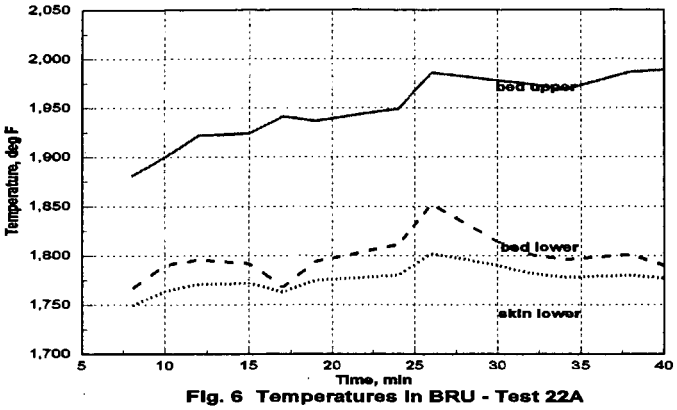


**Fig. 6 Temperatures in BRU - Test 22A**

**Non Adiabatic Gasification of Petroleum Coke**

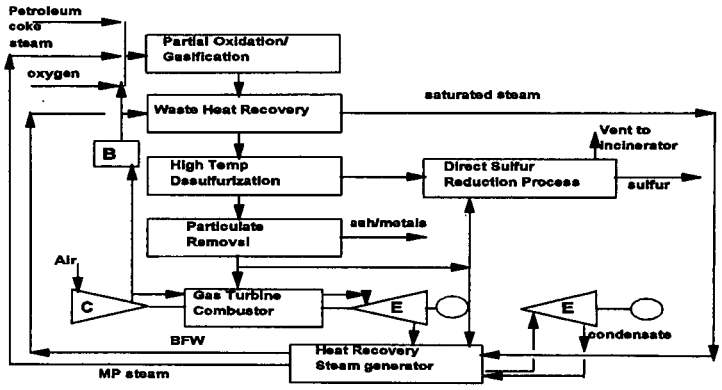


**Figure 7.** Block Flow Diagram for Petroleum Coke Processing